

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Epoxy Fatty Acid Esters and Polyvinyl Resin Compositions containing them

We, SWIFT & COMPANY, a corporation organized and existing under the Laws of the State of Illinois, United States of America, of Union Stock Yards, City of Chicago, State of Illinois, United States of America, do hereby declare the invention, for which we pray that a may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to resin compositions having improved properties and, more particularly, to epoxy fatty acid esters and polyvinyl resin compositions containing them.

Polyvinyl resins, particularly polyvinyl halide resins, are employed in a wide range of applications and in many of these applications it is necessary to plasticize the resin. The physical properties of the resin depend to a great degree upon the amount and type of plasticizer incorporated therein. Usually, while the flexibility, tear resistance, and elongation of vinyls increase with increased plasticizer content, the tensile strength and hardness decrease. Many plasticizers have been employed in the formulation of vinyl resins, and while some of these plasticizers offer advantages in some respects they possess shortcomings in other respects, and this results in the necessity for combinations of two or more plasticizers, each having certain desirable properties that are lacking in some others.

According to the invention there is provided a polyvinyl resin composition comprising a vinyl halide polymer prepared from a monomer, or mixture of monomers of which at least 50% are vinyl halide monomers (units) and oxirane-containing esters of fatty acids of 10—30 carbons and a lower monohydric alcohol, lower dihydric alcohol, lower polyhydric alcohol, benzenoid alcohol, or a mixture thereof, the oxirane groups being present

in the fatty acyl portion of the esters, the oxirane content of the esters being in the range 8.5—12.3%.

The invention also provides esters of higher fatty acids containing 10—30 carbon atoms, the acyl group of the fatty acids containing a plurality of oxirane groups substituted along a fatty chain in an amount sufficient to provide in the esters an oxirane content of about 8.5—12.3%, the alcohol group of the esters being selected from lower monohydric alcohols, lower dihydric alcohols, lower polyhydric alcohols, benzenoid alcohols having less than 10 carbons and mixtures thereof.

The plasticizer compositions of the present invention comprise esters of high oxirane containing fatty acids having 10—30 carbons with mono, di, and polyhydric aliphatic alcohols. These esters are low viscosity oils possessing little or no colour. The esters may be characterized as high oxirane fatty materials containing a plurality of oxirane rings or epoxy groups at those points in the fatty acyl radical which are normally occupied by double bonds in the original non-epoxidized fatty acid or ester.

Monohydric and dihydric alcohol esters of the high oxirane fatty esters which are contemplated include the aliphatic alkyl esters wherein the alcohol portion of the ester is a monohydric alcohol having 1—8 carbons, and aliphatic alcohol esters of dihydric alcohols having 2—6 carbon atoms. Aliphatic alcohols having 8, or less than 8 carbons will be hereinafter referred to as 'lower alcohols' and aliphatic alcohols having more than 8 carbons will be hereinafter referred to as 'higher alcohols'. Lower aliphatic alcohols of the olefin and paraffin series and which may be substituted if desired with non-interfering substituents are suitable. The epoxy fatty acid component is made up of epoxy fatty acids

[Price]

of 10—30 carbons having an oxirane content above about 8.8. Suitable monohydric alcohols providing the alcohol moiety of the ester include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, hexyl, heptyl, and octyl alcohols. Benzenoid alcohols which may be employed in preparing the ester are those benzenoid alcohols having less than 10 carbons and include benzyl, phenyl, 2 - phenylethyl, 1 - phenylethyl and nuclear methylated phenyl alcohols. Dihydric alcohols include the lower glycols, such as ethylene glycol, 1:2 propane diol, 1:3 propane diol, dimethyl ethylene glycol, trimethylene glycol, tetramethylene glycol, and up to hexamethylene glycol. Generally the lower monohydric alcohol esters provide a less viscous dispersion of the vinyl when the resin and plasticizer are mixed than the higher monohydric alcohol esters. The lower alcohol esters are also more volatile than the higher alcohol esters, and therefore for a given preparation a balance between viscosity requirements and volatility requirements is possible by careful selection of the ester. The dihydric and polyhydric alcohol esters act similarly.

Methods for determining the oxirane content of a given high-oxirane ester or mixture of esters are wellknown, and, while the preferred technique is American Oil Chemists Society tentative method Cd—9—57, described in Official and Tentative Methods of the American Oil Chemists Society, Second Edition, 1946, including Additions and Revisions 1947 to 1958, inclusive, other analytical methods known in the art may be employed. The method described by A. J. Durbetaki, Analytical Chemistry, Volume 28, No. 12, December, 1956, pages 2000—2001, is also suitable for determining oxirane content.

The polyhydric alcohol esters of the high oxirane fatty acids include the tri-, tetra-, penta-, and hexahydric alcohol esters of the fatty acid moiety. Included within this group are those aliphatic alcohols having 3—6 carbons and 3 or more alcohol groups. These alcohols include glycerol, erythritol, pentaerythritol, and hexitols, such as mannitol and sorbitol.

The epoxy fatty acid portion of the novel plasticizer is made up of those fatty acids and mixtures of fatty acids having 10—30 carbons and an oxirane content above about 8.8. The saturated acid content of the fatty acid mixture should preferably not exceed about 10—15%. Therefore the presence of such saturated acids as stearic acid, palmitic acid and myristic acid should for best results be held to a minimum. Moreover, the fatty acids should not be hydroxylated or contain conjugated unsaturation. Mixtures containing epoxy-stearic, diepoxystearic, triepoxystearic, diepoxyeicosanoic, triepoxyeicosanoic, diepoxydocosanoic, triepoxydocosanoic, tetraepoxy-

docosanoic and pentaepoxytetracosanoic acids are a very desirable source of the oxirane supplying radical.

Suitable naturally occurring oils which, when substantially completely epoxidized, may be used in practicing the invention are those vegetable and marine triglycerides containing not more than about 10—15% saturated fatty acids and containing unsaturated fatty acids predominantly. These naturally occurring oils should have a degree of unsaturation represented by an iodine value of about 170 to about 205 and the fatty acids are neither hydroxylated nor possess conjugated unsaturation. The linolenic acid oils which are primarily triglycerides of linoleic and linoleic acids are preferred. Among those oils which may be employed are highly epoxidized perilla oil and highly epoxidized linseed oil. These naturally occurring highly unsaturated oils also provide a valuable source of fatty acid mixtures. Purified and concentrated fatty acid mixtures containing a large amount of unsaturated fatty acids may be obtained from such vegetable oils as soybean oil and tall oil, or from the fish oils. These materials must first be refined to concentrate the more highly unsaturated components and remove at least a portion of the saturated acids. The fish oils in particular have a high degree of unsaturation, as represented by iodine values as high as 270, but contain too great a quantity of saturated acids. Therefore these materials are first treated to reduce the saturated acid content below about 10—15%.

In order for the epoxy fatty acid ester to be effective in providing in the esters the desired compatibility, it is necessary that the fatty acid or mixture of fatty acids forming the fatty acyl portion of the ester have an oxirane content above about 8.8 and, as a practical matter, in the range of 8.8—12.3. The preferred oxirane content of the fatty acyl component is around 9.0—9.5. This preferred oxirane content is easily obtained from a mixture of epoxy containing fatty acids containing prior to epoxidation less than about 15% saturated fatty acids and consisting predominantly of the di-, tri-, and tetra-ethenoic acids, a preferred polyvinyl resin composition comprises a vinyl halide polymer prepared from a monomer or mixture monomers of which at least 50% are vinyl chloride monomers and about 4—100 parts based on 100 parts of the polymer of a plasticizer comprising a mixture of lower alkyl alcohol esters of epoxidized fatty acids wherein the mixture comprises esters of epoxidized linoleic acid and epoxidized linolenic acid, the epoxidized linoleic acid comprising not more than about 35% based on the fatty acid mixture, and the combined epoxidized linoleic - linolenic acid content of the mixture comprising more than about 60% of the epoxidized fatty acid mixture, the oxirane content of the mixture being

about 8.8—12.3%. A particularly desirable fatty acid mixture is one containing less than about 35% epoxy linoleic acid and the total epoxy linoleic epoxy linolenic acid content being about 60%. This preferred mixture is readily obtained from naturally occurring linseed oil or perilla oil by subjecting such oils, provided they possess an iodine value above about 170, to an epoxidation treatment such as is described hereinafter.

Those thermoplastic vinyl halide copolymers containing at least 50% of the monomer units as vinyl halide units before polymerization are preferred. The "Vinylite" (Registered Trade Mark) resins, such as "Vinylite" VAGH, "Vinylite" VYHH and "Vinylite" VMCH, and the "Geon" (Registered Trade Mark) resins, such as "Geon" 103 and "Geon" 121, are specific examples of suitable vinyl halide polymers. "Vinylite" VAGH is reported to contain 91% vinyl chloride units, 3% vinyl acetate units, and 6% vinyl alcohol units. "Vinylite" VYHH contains 87% vinyl chloride units and 13% vinyl acetate units. "Vinylite" VMCH contains about 86% vinyl chloride units, 13% vinyl acetate units and 1% maleic acid units. "Geon" 121 and "Geon" 103 contain in excess of 90% vinyl chloride units and generally 96—100% vinyl chloride units.

While the high oxirane content of the epoxy containing material appears to provide a most important advantage in the processing benefits and physical characteristics of products made from the mixture of epoxide and vinyl, the high oxirane content of the epoxy composition combined with a vinyl stabilizer appears to impart extremely high stability to the resin composition. For example, in the production of polyvinyl chloride films from a polyvinyl chloride composition containing a high oxirane fatty ester and a stabilizer comprising an alkaline earth metal salt of a higher aliphatic organic acid, it is possible to operate an extruder for a longer period of time without shutdown and with a minimum amount of burning and charring of the resin composition in the extruder. With conventional vinyls and vinyls plasticized with well-known plasticizers, such as dioctyl phthalate and epoxy plasticizers of less than the minimum oxirane content, it is necessary to frequently shut down extruders being employed to form the vinyl because of an accumulation of charred resin in the extruder resulting from heat degradation. Specific stabilizers which may advantageously be employed include zinc octoate, preferably zinc salts of higher C8—C18 aliphatic organic acids, barium octoate, calcium octoate, and mixtures of barium-cadmium salts of fatty acids, such as barium-cadmium laurate or barium-cadmium stearate. Still other stabilizers are the typical vinyl stabilizers, such as dibutyl tin dilaurate, zinc dilaurate, the lead carbonates and stearates,

and barium-cadmium phosphites. A particularly valuable stabilizer mixture employed in the compositions of the present invention is a mixture of zinc and calcium stearates. This composition is unusually valuable because it appears to inhibit heat degradation while imparting improved lubricating qualities to the polyvinyl chloride resin. Moreover, it is sufficiently non-toxic for the film to be used in wrapping foods.

Fillers, pigments, lubricants, antistatic agents and antiblocking agents may also be employed in the composition where desirable. A particularly effective static reducer is the product resulting from the condensation of 1 mol of tetraethylene pentamine with 5 mols of stearic acid.

The following Examples illustrate the invention.

#### *Epoxidation of Unsaturated Fatty Acid Esters or Mixtures Thereof.*

Inasmuch as heavy metals deleteriously affect the epoxidation reaction, it is advisable to conduct the epoxidation in glass equipment or in carefully prepared metal reaction vessels. The metal equipment should be conditioned by nitric acid passivation before the first use to remove welding beads, metal filings, and other sources of heavy metal contamination. Also the reactants should be free of heavy metals. The procedures which are described hereafter were conducted in 316 stainless steel equipment.

#### EXAMPLE I.

A benzene solution comprising 780 lbs. benzene and 850 lbs. linseed oil is charged to the reaction vessel and the solution is vigorously agitated as 525 lbs. of 50% hydrogen peroxide is added. The sulphuric acid catalyst (5.3 lbs.) is diluted with 5 lbs. of peroxide, and this mixture is then added to the reaction vessel. The well agitated mixture is then heated to 145°F. and 90% formic acid is slowly added to the heated mixture. The reaction is exothermic and the temperature is permitted to rise to about 160—162°F., at which time cooling is employed to maintain this approximate temperature. The addition of 45 lbs. of formic acid requires about 2 hours. The total reaction time including this 2-hour addition period is about 9 hours, and the reaction temperature ranges between 160—168°F. After cooling, the aqueous layer of the product is drawn off and the remaining benzene layer is washed several times with hot water until the wash solution is neutral. Usually about 6 or 7 washes are required. A purification step may be interposed at this point. The purification involves agitating a mixture of the washed benzene layer and 80 lbs. water containing 8 lbs. sodium hydroxide or other alkaline refining agent for 1 hour while maintaining the temperature at about 150°F.

Benzene is then removed by distillation at atmospheric pressure, the final traces being removed under vacuum. Physical constants of the starting linseed oil and the epoxidized product are as follows:

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	Feed Analysis	Epoxidized Product
Iodine value	182.0	4.57
Sap. No.	193.0	175.5
F.F.A.	0.39	0.09
Gardner colour	4	4
Gardner viscosity	A	T—U
Peroxide No.	1.05	26.4
% Oxirane	0.0	9.1
Moisture and vapour	0.03	0.19

#### EXAMPLE II.

10 The preparation of the lower alkyl esters is as follows: Linseed oil is reacted with the appropriate lower monohydric alcohol by refluxing the alcohol containing potassium hydroxide with the oil. The glycerol which is freed in the ester interchange is drawn off, and more alcoholic caustic is added to the reaction mixture and refluxing continued. After 15 3 passes of alcoholic alkali the free glycerol content of the product is less than 0.3%. The first pass with the primary alcohol involves

about 30% by weight of the alcohol based upon the linseed oil while the 2 subsequent passes involve the use of about 50% by weight of the alcohol. Epoxidation of the monohydric alcohol esters of the linseed oil fatty acids is carried out in the manner of Example I. The methyl, ethyl, propyl, *n*-butyl, isobutyl, *n*-octyl and benzyl esters of epoxidized linseed oil fatty acids were prepared. The physical constants of these esters is as follows:

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Ester of Linseed Oil Fatty Acids	Initial I.V.	Final I.V.	% Total Glycerol	% Oxirane content of linseed oil fatty acids	% Oxirane of ester
1. methyl	185	7.2	0.04	9.15	8.9
2. ethyl	180	8.0	0.03	9.0	8.5
3. propyl	161	7.1	0.20	8.95	7.9
4. <i>n</i> -butyl	154.5	7.4	0.07	8.97	7.6
5. isobutyl	156.5	8.5	0.04	8.85	7.5
6. <i>n</i> -octyl	130	12.8	0.10	8.80	6.44
7. Benzyl	145	7.3	—	8.5	7.1

The benzyl ester was prepared from the acid chloride of the linseed acid mixture and benzyl alcohol in pyridine. It was epoxidized in the manner of Example I.

The upgrading or concentration of more unsaturated fatty acids and the removal of the more saturated fatty acid components from naturally occurring fatty acid esters and fatty alcohols and mixtures thereof follows:

### EXAMPLE III.

Linseed oil fatty acids are prepared by saponifying linseed oil with alcoholic alkali; in the present case a methanol solution of sodium hydroxide was employed. Upon neutralization and removal of the fatty acid component, a mixture containing 47% linolenic, 17% linoleic, 27% oleic, and 9% saturated fatty acids was obtained. 1,000 Grams of this mixed fatty acid composition was added to a hot solution of 2,000 grams of urea in 5 litres of methanol. The methanol solution of urea was agitated vigorously during addition of the

fatty acids. A precipitate formed and the mixture was allowed to stand overnight at room temperature. The precipitated urea complexes were then filtered off and discarded while the filtrate was distilled under vacuum to remove the major portion of methanol. The fatty acid mixture derived from the filtrate was then washed with water to remove excess urea. After drying, the product which consisted of 425 grams of an oily liquid was analyzed. It was found to have an iodine value of 241 as compared with an iodine value of the mixture of fatty acids prior to the urea treatment of 181.4.

This urea fractionation technique was also employed in the treatment of soybean oil fatty acids and tall oil fatty acids. The composition of the fatty acid mixtures follows:

Analytical Data	Soybean Oil		Distilled Tall Oil	
	Original oil	After urea treatment	Original oil	After urea treatment
Iodine value of fatty acid mixture	123.0	190.7	124.2	169.4
% Linolenic acid	6.8	19.0	—	—
% Linoleic acid	40.7	76.4	47.0	90.2
% Oleic acid	39.9	3.5	45.0	9.0
% Saturated acid	11.9	1.1	7.0	0.8

The yield of highly unsaturated soybean oil fatty acids was 35%, while the yield of highly unsaturated tall oil fatty acids was 51%. Other methods of concentrating unsaturated fatty acids are known in the art.

Each of the fractionated fatty acid mixtures noted above was esterified with *n*-butanol in the following manner: A mixture of 500 grams of the fatty acids and 250 grams of *n*-butanol was heated, along with 10 grams of *p*-toluene sulphonic acid, in a glass vessel fitted with a reflux condenser

and a water trap for a time sufficient to remove the theoretical amount of water. A water trap reflux condenser equipped with a calibrated receiver is suitable for this purpose. After the theoretical amount of water had been accumulated in the trap, the reaction mixture was cooled, washed with a 5% aqueous solution of sodium carbonate, and finally washed with water until the washings were neutral to litmus. The excess alcohol was steam distilled from the ester and, after drying, the product was analyzed.

Butyl Ester of	Saponification No.	Iodine Value	Acid Value
Linseed oil fatty acids	164.9	205.0	0.93
Soybean oil fatty acids	167.4	160.1	0.39
Tall oil fatty acids	165.9	143.9	0.65

After epoxidation of these butyl esters in accordance with the procedure described in Example I, the final epoxidized esters had the following physical characteristics:

Butyl Ester of	Saponification No.	Acid No.	Iodine Value	% Oxirane Oxygen
Linseed oil fatty acids	148.7	1.10	7.6	9.89
Soybean oil fatty acids	151.0	0.41	4.9	7.93
Tall oil fatty acids	152.0	0.63	3.2	7.47

It will be noted that, while the percent oxirane oxygen for the butyl esters is less than 8.8, the percent oxirane oxygen in the fatty acid is well above this lower limit. These compositions are most effective, particularly as regards handling characteristics and the provision of superior low temperature flexibility characteristics in films prepared from vinyl halide resins containing these lower alkyl esters of mixed epoxidized fatty acid esters.

Flexible films which are prepared from the vinyl resin-high oxirane composition exhibit substantial freedom from plasticizer migration and exudation and also possess highly desirable handling characteristics. These films are prepared by well-known milling, calendering or extruding techniques. It is possible, because of the unexpectedly high compatibility of the epoxide and resin, to employ the high oxirane fatty ester as the sole plasticizer for the vinyl resin to obtain the desired flexibility. Moreover, troublesome heat degradation of the polyvinyl halide is held to a minimum by the plasticizer. This improved resistance to heat-induced deterioration allows

for the omission of stabilizer compositions, such as the metal salts mentioned previously. This ability to dispense with metal salt stabilizers is most important in the preparation of food films, since films designed for use in the packaging of foods should be free from extractable toxic metal salts and other toxic substances.

The effect of varying amounts of the plasticizer on milled films prepared from the vinyl halide-high oxirane mixture is shown in Example IV which follows:

#### EXAMPLE IV.

A calendering type polyvinyl chloride resin (Geon 103 EP, a product of B. F. Goodrich Co., Cleveland 15, Ohio) containing 90% or more vinyl chloride units in the monomer mixture was admixed with varying proportions of epoxidized linseed oil (oxirane content 9.2%) in a Hobart mixer to form dry blends. The high oxirane composition was varied in increments of 5 parts. One part of zinc stearate was added to each batch having less than 60 parts of the high oxirane compound. The formulation is as follows:

Polyvinyl chloride (Geon 103 EP)	100 parts
Epoxidized linseed oil	X parts
Zinc stearate	1 part

Each of the dry blends was milled at 320°F. for 5 minutes and films of 2—4 mils thickness were taken for determination of the physical data for each. The following table

shows the physical data for films prepared from mixes containing varying amounts of the epoxide.

Parts Epox- idized Linseed Oil in Above Formulation	Ultimate Tensile Strength psi	Corrected Elongation at Break percent	Modulus at 100% Elongation psi	Weatherometer Stability*
25	4700	10	—	613 hrs.
30	3850	65	—	629 "
35	3200	180	3150	654 "
40	3200	205	2950	660 "
45	2900	195	2600	665 "
50	3000	200	2600	723 "
55	2800	210	2300	735 "
60	2500	215	1900	792 "
65	2300	215	1650	827 "
70	2000	225	1450	757 "
75	1800	250	1400	810 "

\* An Atlas Sunshine-Carbon Arc type weatherometer Model XW was employed.

#### EXAMPLE V

Extruded films were prepared from formulations containing varying levels of the high oxirane linseed oil. The dry blend of the resin plasticizer compound was pelletised and the pellets were fed to an extruder which produced the film in the form of an inflated tube. The formula for the dry blend is as follows:

Polyvinyl chloride (Geon 103 EP)	100 parts
Epoxidized linseed oil	X parts
Calcium-zinc stearate (Harshaw 59—V—11)	2 parts
Mineral oil	0.9 parts

The films prepared showed the following physical properties:

Parts Epox- idized Linseed Oil in Above Formulation		Ultimate Tensile Strength	Corrected Elongation at Break	Modulus at 100% Elongation	Tearing Force
		psi	percent	psi	g/mil
20	L	7300	5	—	21
	T	7200	5	—	11
30	L	5700	130	5300	80
	T	5300	150	4800	96
40	L	4000	210	3700	136
	T	4100	210	3700	114

L — indicates the values measured in the longitudinal direction of the film.

T — indicates the values measured in the transverse direction of the film.

#### EXAMPLE VI

Milled films were prepared from the following compositions which were formulated as dry blends in the mixer:

Polyvinyl chloride (Geon 103 EP)	100 parts
Butyl ester epoxidized linseed oil fatty acids	X parts
Barium-cadmium laurate stabilizer	2 parts
Chelating compound	1 part

Mixture was milled for 5 minutes at 340° F.

Parts Butyl Ester Epoxidized Linseed Oil Fatty Acids	Longitudinal		Transverse	
	Ultimate Tensile Strength	Corrected Elongation at Break	Ultimate Tensile Strength	Corrected Elongation at Break
	psi	percent	psi	percent
0	7500	9	8400	10
4	7900	4	7900	3
8	7100	3	7000	3
12	6500	5	6200	3
16	5100	10	4800	7



It was noted that the sample containing 4 parts butyl ester can be processed much more easily than the sample containing no plasticizer. While elongation and tensile strength

are not greatly affected by the plasticizer, the heat stability of the mix is improved significantly.

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### EXAMPLE VII

The following ingredients were dry blended in a Hobart mixer:

Polyvinyl chloride	100 parts
Epoxidized linseed oil (9.2% oxirane oxygen)	40 parts
Zinc octoate	1 part
Static reducer*	2 parts
Mineral oil	$\frac{3}{4}$ part

\* 1 mol of tetraethylene pentamine mixed with 5 mols of stearic acid and heated to a temperature of 180° C. for about 2 hours.

The formulation is extruded to provide thin films of about 1—10 mils thickness. The film is clear, transparent and glossy, and has very good flexibility as well as freedom from static. The polyvinyl chloride composition exhibits very desirable handling characteristics, and there is a minimum of burning and charring in the extruder. This resistance to heat degradation results primarily from the superior stability of the formulation.

#### WHAT WE CLAIM IS:—

1. A polyvinyl resin composition comprising a vinyl halide polymer prepared from a monomer or mixture of monomers of which at least 50% are vinyl halide monomers and oxirane-containing esters of fatty acids of 10—30 carbons and a lower monohydric alcohol, lower dihydric alcohol, lower polyhydric alcohol, benzenoid alcohol, or a mixture thereof, the oxirane groups being present in the fatty acyl portion of the esters, the oxirane content of the esters being in the range 8.5—12.3%.

2. A polyvinyl resin composition comprising a polyvinyl chloride polymer prepared from a monomer or mixture of monomers of which at least 50% are vinyl chloride monomers and lower aliphatic alcohol esters of epoxidized fatty acids, the fatty acids containing sufficient oxirane oxygen to provide in the esters an oxirane content of 8.5—12.3%.

3. A polyvinyl resin composition comprising a vinyl halide polymer prepared from a monomer or mixture of monomers of which at least 50% are vinyl halide monomers and lower alkyl alcohol esters of epoxidized lin-

seed oil fatty acids, the oxirane content of the fatty acids being about 8.8—12.3%.

4. A polyvinyl resin composition comprising a vinyl halide polymer prepared from a monomer or mixture of monomers of which at least 50% are vinyl halide monomers and glyceryl esters of epoxidized linseed oil fatty acids, the oxirane content of the fatty acids being about 8.8—12.3%.

5. A polyvinyl resin composition comprising a vinyl halide polymer prepared from a monomer or mixture of monomers of which at least 50% are vinyl halide monomers and lower monohydric alcohol esters of epoxidized linseed oil fatty acids, the oxirane content of the fatty acids being about 8.8—12.3%.

6. A polyvinyl resin composition comprising a polyvinyl chloride polymer prepared from a monomer or mixture of monomers of which at least 50% are vinyl chloride monomers and lower dihydric alcohol esters of epoxidized linseed oil fatty acids, the oxirane content of the fatty acids being about 8.8—12.3%.

7. A polyvinyl resin composition comprising a vinyl halide polymer prepared from a monomer or mixture of monomers of which at least 50% are vinyl halide monomers and lower polyhydric alcohol esters of epoxidized linseed oil fatty acids, the oxirane content of the fatty acids being about 8.8—12.3%.

8. A polyvinyl resin composition comprising a vinyl halide resin prepared from a monomer or mixture of monomers of which at least 90% are vinyl chloride monomers and a plasticizer, the plasticizer being a mixture of lower alkyl alcohol esters of epoxidized fatty

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acids wherein the mixture comprises esters of epoxidized linoleic acid and epoxidized linolenic acid, the epoxidized linoleic acid comprising less than about 35% based on the fatty acid mixture, and the combined epoxidized linoleic-linolenic acid content of the mixture comprising more than about 60% based on the fatty acid mixture, the oxirane content of the epoxidized fatty acid mixture being about 8.8—12.3%.

9. A polyvinyl resin composition comprising a polyvinyl chloride resin prepared from a monomer or mixture of monomers of which at least 50% are vinyl chloride monomers and an epoxidized fatty acid ester plasticizer, the ester plasticizer being a mixture of lower alkyl alcohol esters of fatty acids wherein the mixture comprises esters of epoxidized linoleic acid and epoxidized linolenic acid, the epoxidized linoleic acid comprising not more than about 35% based on the fatty acid mixture, and the combined epoxidized linoleic-linolenic acid content of the mixture comprising more than about 60% based on the fatty acid mixture, the oxirane content of the fatty acid mixture being about 8.8—12.3%.

10. A polyvinyl resin composition comprising a polyvinyl chloride polymer prepared from a monomer or mixture of monomers of which at least 50% are vinyl halide monomers having admixed therewith a mixture of lower alkyl esters of epoxidized fatty acids, the fatty acids comprising not more than 35% epoxidized linoleic acid and at least 60% epoxidized linoleic-linolenic acids, the mixture of esters having an oxirane content of 8.5—12.3%.

11. A polyvinyl resin composition comprising a vinyl halide resin prepared from a monomer or mixture of monomers of which at least 50% are vinyl chloride monomers, a mixed ester plasticizer, the plasticizer being a mixture of lower alkyl alcohol esters of epoxidized fatty acids wherein the mixture comprises esters of epoxidized linoleic acid and epoxidized linolenic acid, the epoxidized linoleic acid comprising not more than 35% based on the fatty acid mixture, and the combined epoxidized linoleic-linolenic acid content of the mixture comprising more than about 60% based on the epoxidized fatty acid mixture, the oxirane content of the mixture being about 8.8—12.3%, and as a stabilizer a zinc salt of a higher C8—C18 aliphatic organic acid.

12. A polyvinyl resin composition comprising a vinyl halide polymer prepared from a monomer or mixture of monomers of which at least 50% are vinyl chloride monomers and about 4—100 parts based on 100 parts of the polymer of a plasticizer comprising a mixture of lower alkyl alcohol esters of epoxidized fatty acids wherein the mixture comprises esters of epoxidized linoleic acid and epoxidized linolenic acid, the epoxidized linoleic acid comprising not more than about 35% based on the fatty acid mixture, and the combined epoxidized linoleic-linolenic acid content of the mixture comprising more than about 60% of the epoxidized fatty acid mixture, the oxirane content of the mixture being about 8.8—12.3%.

13. Esters of higher fatty acids containing 10—30 carbon atoms, the acyl group of the fatty acids containing a plurality of oxirane groups substituted along a fatty chain in an amount sufficient to provide in the esters an oxirane content of about 8.5—12.3%, the alcohol group of the esters being selected from lower monohydric alcohols, lower dihydric alcohols, lower polyhydric alcohols, benzenoid alcohols and having less than 10 carbons and mixtures thereof.

14. An ester of oxirane fatty acids and a lower aliphatic alcohol, the fatty acids being substituted along the acid chain with oxirane groups sufficient to provide in the acid an oxirane content of about 8.8—12.3%, the lower aliphatic alcohol being an alcohol of the olefin and paraffin series having 1—8 carbons.

15. An ester of oxirane-containing fatty acids having 10—30 carbons and aliphatic alcohols having 3—6 carbons and three or more alcohol groups, the fatty acids having sufficient oxirane groups to provide in said acid an oxirane content of about 8.8—12.3%.

16. A resin composition substantially as hereinbefore described with reference to any one of Examples IV to VII.

17. A process for the preparation of an ester as claimed in claim 13, substantially as hereinbefore described with reference to Example I, II or III.

18. An ester prepared by a process as claimed in claim 17.

SWIFT & COMPANY,  
Per: Boulton, Wade & Tennant,  
111/112, Hatton Garden, London, E.C.1.  
Chartered Patent Agents.